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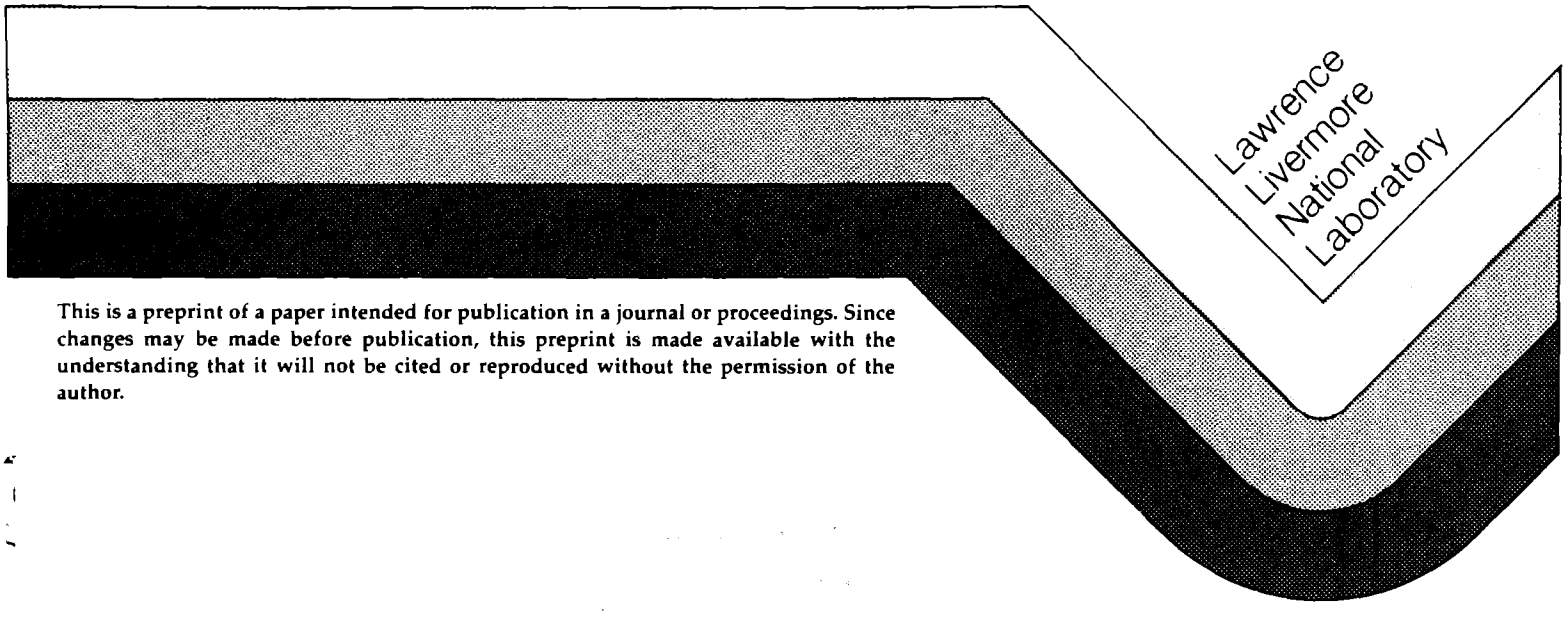

CALCULATION OF THE NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF $YBa_2Cu_3O_{7-x}$[§]

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Nuclear quadrupole resonance[1,2] (NQR) and nuclear magnetic resonance[3] (NMR) studies on $^{63,65}Cu$ have demonstrated that the resonance properties of these nuclei can give important information about the electronic structure of the high temperature superconductor $YBa_2Cu_3O_{7-x}$ as well as the exchange coupling energy between the Cu(2) sites.[4] Measurements for various oxygen stoichiometries have given insight into the effect of oxygen content on the valence state of the Cu.[5]

In the work reported here, the electric field gradient (EFG) tensors at the Cu(1) and Cu(2) sites in $YBa_2Cu_3O_{7-x}$, have been determined from calculations on large clusters for x=0 and 1. The results were found to be sensitive to the nature of the chemical bonding at the Cu sites and indicate that point-charge models which neglect the valence electron contributions will not accurately describe the EFG. Good agreement with experiment is obtained only if the multi-valent character of the Cu ions was included in the wavefunction by configuration interaction.

A description of the basic approach used in these cluster calculations has been given in previous studies of Cu^+ in NaF and NaCl lattices.[6,7] For $YBa_2Cu_3O_{7-x}$, the Cu ion of interest and its nearest-neighbor oxygen ions were surrounded by atoms whose valence electrons were explicitly treated. These clusters were then embedded in a larger point charge lattice which reproduced the correct shape of the crystal field at the Cu site. All electrons on the Cu(1) or Cu(2) site were explicitly included in the calculation in order to allow for core polarization due to the surrounding ions. A flexible Gaussian basis set[8] was used for the all-electron Cu and the [Ar] core electrons of the boundary Cu ions were replaced by an effective core potential (ECP)[9] with the valence basis functions optimized for the Cu^{+2} ion. Pacios and Christiansen's[10] ECP and basis set were used on the nearest-neighbor oxygen ions and reoptimized for the O^{-1} free ion. The [Kr] core of Y and the [Xe] core of Ba were also replaced by ECP's.[11]

The NQR frequencies calculated from the EFG tensors and the experimental ^{63}Cu quadrupole moment[12] are given in Table I for the Cu(1) and Cu(2) sites of $YBa_2Cu_3O_6$. The ratio of the experimental NQR frequency of ~30 MHz[2,5] to the calculated frequency of 40 MHz is 0.74.

Table I. Comparison of the calculated Cu NQR frequencies to experiment for $YBa_2Cu_3O_6$ (units are MHz)

Cu(1)	Theory $\|3d^{10}\rangle$	Refs. 2,5	Ratio
ν_{xx}	-20.2	--	
ν_{yy}	-20.2	--	
ν_{zz}	40.5	±30	0.74

Cu(2)	Theory $\|3d^9\rangle$	Theory $\|3d^{10}\underline{L}\rangle$	Theory 72%$\|3d^9\rangle$, 28%$\|3d^{10}\underline{L}\rangle$	Ref. 13	Ratio
ν_{xx}	-26.2	14.8	-14.7		
ν_{yy}	-26.2	14.8	-14.7		
ν_{zz}	52.5	-29.7	29.5	±22	0.74

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We believe this error is mainly due to limitations of the basis set. For the Cu(2) site the NQR frequency was calculated for both the $|3d^9\rangle$ and $|3d^{10}\underline{L}\rangle$ configurations. An experimental frequency of ~22 MHz has been obtained by Yasuoka *et al.*[13] from antiferromagnetic resonance (the absolute sign in all the experimental measurements discussed here has not been determined). The EFG for the $|3d^9\rangle$ configuration substantially overestimates the NQR frequency, however by including configuration interaction with the $|3d^{10}\underline{L}\rangle$ state, it is possible to obtain a value consistent with the error found for the Cu(1) site.

The results for x=0 are compared to the measurements of Pennington *et al.*[3] on magnetically aligned samples in Table II.

Table II. Comparison of the calculated Cu NQR frequencies to experiment for $YBa_2Cu_3O_7$ (units are MHz)

Cu(1)		Theory		Scaled	Ref. 1
	$\|3d^8\rangle$	$\|3d^9\underline{L}\rangle$			
ν_{xx}	76.3	25.4		19.0	19.0
ν_{yy}	-41.8	-31.3		-23.5	-19.2
ν_{zz}	-34.5	5.9		4.4	0.2
NQR	76.4	-33.3		-24.9	-22.0

Cu(2)		Theory		Scaled	Ref. 1
	$\|3d^9\rangle$	$\|3d^{10}\underline{L}\rangle$	88%$\|3d^9\rangle$, 12%$\|3d^{10}\underline{L}\rangle$		
ν_{xx}	-25.9	16.9	-20.6	-15.4	-15.8
ν_{yy}	-26.6	16.9	-21.2	-15.9	-15.8
ν_{zz}	52.5	-33.9	41.7	31.3	31.5
NQR	52.5	-33.9	41.7	31.3	31.5

For site 1 it is clear that the theoretical results agree with experiment only if Cu is described by the $|3d^9\underline{L}\rangle$ configuration ($\underline{L}$ is not necessarily constrained to be a near-neighbor ligand hole but can reside in the CuO_2 plane). After applying the 0.74 scale factor determined from the Cu(1) x=1 calculation, the agreement with the experimental tensor is good. As for $YBa_2Cu_3O_6$, site 2 must be described by a mixture of the $|3d^9\rangle$ and $|3d^{10}\underline{L}\rangle$ configurations in order to reproduce the measured tensor. However, the weight of the hole on the O-site is considerably reduced.

The calculations have shown that the Cu(1) site in $YBa_2Cu_3O_6$ is $3d^{10}$ and in $YBa_2Cu_3O_7$ is $3d^9$. For both materials the Cu(2) site is predominately $3d^9$ but with a significant mixture of the $3d^{10}\underline{L}$ configuration.

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